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TOLYLENE-2,4-DIISOCYANATE (2,4-TDI) - DETERMINATION OF PHYSICOCHEMICAL PROPERTIES, WITH COVER LETTER DATED 3/27/96

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March 27, 1996

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ATTN: 8(d) Health and Safety Reporting Rule
(Notification / Reporting)

SUBJECT: TSCA SECTION 8(D), HEALTH AND SAFETY DATA REPORTING

As required by Toxic Substances Control Act, Section 8(d), Shell is submitting copies of health and safety studies as outlined in 40 CFR 716. Five reports are enclosed (Report Numbers 514, 515, 516, 517 and 518). Each individual study is accompanied by a cover page as requested under 716.7(b). An index is also enclosed which includes the study title, date, specific chemical substance, CAS number, and Shell's report reference number for ease of future identification.

The studies are no longer considered CBI, per Marilyn Burton-Jones of Shell

Sincerely,

J. C. Willett
Manager, Product Safety and Compliance
Oil and Chemical Products
Health, Safety and Environmental

/MSBJ
Enclosures

INDEX OF HEALTH AND SAFETY STUDIES SUBMITTED TO EPA
SORTED BY SUBMISSION NUMBER

SUB. NO.	TITLE	RPT. DATE	CHEMICAL	CAS NUMBER	SHELL REF.
514	DETERGENT TREATABILITY STUDIES.IV ANERARCBIC EXPERIMENTS	870900	4-NONYL PHENOL	000104-40-5	WRC 117-87
515	ORTHO TERTBUTYLPHENOL: SKIN AND EYE IRRITANCY.	890307	2-TERT BUTYLPHENOL	000088-18-6	SBGR.88.269
516	O-TERT.BUTYL PHENOL: ACUTE ORAL AND DERMAL TOXICITY, AND SKIN SENSITISATION POTENTIAL	901119	2-TERT BUTYLPHENOL	000088-18-6	SBGR.90.123
517	BACTERIAL MUTAGENICITY STUDIES WITH ORTHO-TERTBUTYLPHENOL	890123	2-TERT BUTYLPHENOL	000088-18-6	SBGR.88.240
518	TOLYLENE-2,4-DIISOCYANATE (2,4-TDI): DETERMINATION OF PHYSICOCHEMICAL PROPERTIES	950825	TOLYLENE-2,4-DIISOCYANATE	000584-84-9	SBER.94.004

REPORT NO. 518

SUBMISSION OF COPIES OF HEALTH AND SAFETY STUDIES - TSCA SECTION 8(D)

CHEMICAL NAMES OF LISTED SUBSTANCES	CAS NUMBER(S)
TOLYLENE-2,4-DIISOCYANATE	000584-84-9

STUDY TITLE: TOLYLENE-2,4-DIISOCYANATE (2,4-TDI): DETERMINATION OF PHYSICOCHEMICAL PROPERTIES

STUDY REFERENCE: SBER.94.004

SUBMITTED BY:

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EXTERNAL REPORT

SBER.94.004

Tolylene-2,4-diisocyanate (2,4-TDI): Determination of physicochemical properties

Fisk PR
Langner EJ

Contains No CBI

SECURITY CLASS:

DOCUMENT TYPE:	EXTERNAL REPORT	
DOCUMENT NUMBER:	SBER.94.004	
TITLE:	Tolylene-2,4-diisocyanate (2,4-TDI): Determination of physicochemical properties	
AUTHOR(S):	Fisk PR	SE/1
	Langner EJ	SE/1
REVIEWED BY:	Lyne RL	SE/1
PARTICIPANT(S):	Sherren JA	SE/1
PROJECT NUMBER:	-	
SUB PROJECT:	6205	
PROJECT TITLE:	-	
SPONSOR:	-	
BUDGET CODE:	-	
SOURCE:	Shell Research Limited, Sittingbourne Research Centre.	
ORIGINATING DEPT:	Safety and Environmental Research Department	
DATE:	September 1995	

PF/792

SBER.94.004

Study Title

Tolylene-2,4-diisocyanate (2,4-TDI): Determination of physicochemical properties

Regulatory Data Requirement

EEC Tests, A1, A2, A3, A4, A14

Authors

P.R. Fisk
E.J. Langner

Study Completed On

25th August 1995

Performing Laboratory

Sittingbourne Research Centre,
Sittingbourne, Kent ME9 8AG, U.K.

Laboratory Project Identity

Study No. 6205 Report No. SBER.94.004

(Total number of pages in the study: 33)

This page is reserved for information relevant to regulatory submission.

COMPLIANCE WITH GOOD LABORATORY PRACTICE

This study has been conducted in compliance with GOOD LABORATORY PRACTICE and meets the following requirements:

United Kingdom Department of Health, Principles of Good Laboratory Practice LONDON 1989

Organisation for Economic Co-operation and Development Principles of Good Laboratory Practice PARIS 1982

except that no claim of GLP compliance is made in respect of the test substance characterisation data provided by the supplier of the test substance, reported in Appendix B.

This report fully and accurately reflects the raw data generated in the study.

Study Director:

P. R. Fish — (Signature)

25/8/95 — (Date)

QUALITY ASSURANCE STATEMENT

REPORT NUMBER: SBER.94.004

STUDY NUMBER: 6205

REPORT TITLE: Tolylene-2,4-diisocyanate (2,4-TDI): Determination of physicochemical properties

STUDY DIRECTOR: P.R. Fisk

The conduct of this study was inspected on the dates given below. In addition, routine procedures carried out in all studies of this type have been inspected at intervals according to a predetermined schedule and the relevant dates are also given below.

This report has been audited to ensure that it accurately describes the methods used and that the reported results accurately reflect the raw data of the study.

Date of inspection or audit	Date of QA report to management
16.02.94	16.02.94
18.02.94	28.02.94
25.03.94	25.03.94
13.04.94	15.04.94
19.07.95	19.07.95

Jane M Gilbert
29th August, 1995

J.M. Gilbert
QUALITY ASSURANCE UNIT

SBER.94.004

THE DEPARTMENT OF HEALTH OF THE GOVERNMENT OF THE UNITED KINGDOM

GOOD LABORATORY PRACTICE

STATEMENT OF COMPLIANCE

IN ACCORDANCE WITH DIRECTIVE 88/320 EEC

LABORATORY

Shell Research Limited
Sittingbourne Research Centre
Sittingbourne
Kent
ME9 8AG

DATE OF INSPECTION

17 August 1992

A general inspection for compliance with the Principles of Good Laboratory Practice was carried out at the above laboratory as part of the UK GLP Compliance Programme.

At the time of the inspection no deviations were found of sufficient magnitude to affect the validity of studies performed at these facilities.

D.F. Moore

30/10/92 D. F. Moore
Director
UK GLP Monitoring Unit

CHRONOLOGY OF STUDY

Study initiation date	16th February 1994
Testing start date	2nd March 1994
Testing end date	11th May 1994

LOCATION of Raw Data, Specimens and Final Report:

Sittingbourne Research Centre
Sittingbourne, Kent ME9 8AG
U.K.

Tolylene-2,4-diisocyanate (2,4-TDI): Determination of physicochemical properties

(Study Number: 6205)

SUMMARY:

Physicochemical properties of tolylene-2,4-diisocyanate (2,4-TDI) have been determined in accordance with the test methods described in the Official Journal of the EEC. The results obtained were as follows:

Freezing point:	(A1)	21°C
Boiling point:	(A2)	252 to 254°C at 1011 hPa
Relative density at 25°C:	(A3)	$D_4^{25} = 1.214$
Vapour pressure (calculated)	(A4)	1.5 Pa at 20°C
(measured)		2.1 Pa at 20°C
Explosivity:	(A14)	Not explosive

The test references are given in parentheses.

C.J. Kroese, Manager & Director Research,
Shell Research Limited,
Sittingbourne Research Centre,
Sittingbourne, Kent, ME9 8AG, U.K.

Date : 28/9/94.

TEXT:

CONTENTS

PROFESSIONAL AND SUPERVISORY PERSONNEL INVOLVED IN STUDY

Scientific Reviewer: R.L. Lyne

STUDY DIRECTOR: P.R. Fisk

P. R. Fisk
(Signature)

25/8/95
(Date)

1. INTRODUCTION

Determination of the physicochemical properties of tolylene-2, 4-di[illegible]anate (2,4-TDI) has been requested for regulatory purposes. The studies have been pe[illegible]med in accordance with the test methods described in the Official Journal of the European Communities(1). The study protocol is given in Appendix A.

2. MATERIALS AND METHODS

The standard test reference numbers are given in parentheses.

2.1 Description of the test substance

Tolylene-2,4-diisocyanate (abbreviated to 2,4-TDI) was received from Rhone-Poulenc via the Sittingbourne Research Centre Test Substance Unit. It has an overall purity of 99.9%; further details on its composition are given in Appendix B.

2.2 Determination of the freezing point of 2,4-TDI (A1)

An estimate of the melting point/freezing point was available from the test substance data sheet, which was 22°C.

2.2.1 Equipment

a. Crystallizing point apparatus: a glass test tube of nominal size 150 mm by 25 mm was placed inside another glass test tube of nominal size 160 mm by 38 mm. The outer tube was flanged so that it could be supported by a metal cover plate. The assembly was placed centrally in a 1000 ml tall form beaker. The outer tube was weighted with lead shot, and the inner tube was closed by means of a cork which carried a glass stirrer, and, through its centre, an appropriate thermometer. A second thermometer was placed in the beaker.
b. Stop clock.
c. Alcohol in glass thermometers.

2.2.2 Method

The beaker was filled with cooling medium (ice-water at ca. 14°C) to within 20 mm of the top. The sample of test substance was pre-heated to form a melt. The inner tube was removed from the apparatus and approximately 10 ml of melted sample was added. The cork carrying the thermometer and glass stirring rod was inserted and the inner tube replaced in the crystallizing point apparatus. The sample was gently and continuously stirred and the temperature of the sample and cooling medium were recorded at intervals of 30 seconds, until the temperature remained constant for five consecutive readings. This

temperature is the freezing point.

The experiment was duplicated.

2.3 Determination of the boiling point of 2,4-TDI (A2)

The boiling point of 2,4-TDI has been determined using the Siwoloboff method. Information about boiling was also obtained from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These were used primarily for tests of thermal stability, described in Section 2.6.

The apparatus (approximate dimensions) used consisted of:
A glass tube, 90 mm long, 5 mm i.d., sealed at the lower end
A glass capillary, 100 mm long, 1 mm i.d., sealed at the upper end.
A mercury in glass thermometer.
A heating bath (a conical flask containing silicone oil, with a side arm)
A magnetic stirrer hotplate.
A barometer.

The procedure used was as follows:

1. The sample tube was filled with the test substance, and the capillary was placed into the tube with its open end at the bottom.
2. The tube assembly and the thermometer were fixed together by a small band, and placed in the side arm of the conical flask.
3. The level of silicone oil in the heating bath was sufficient to be above the level of the sample.The bath was heated at 3°C per minute up to 10°C below the expected boiling point, and then at 1°C per minute.
4. When a stream of bubbles was observed emerging from the capillary the temperature was noted and the source of heating was removed from the bath.
5. The temperature at which the test substance re-entered the capillary was recorded.
6. The ambient pressure was measured using an electronic barometer (Prosser Weathertrend), and recorded.

The experiment was duplicated.

2.4 Determination of the density of 2,4-TDI (A3)

An automated method to measure the density of liquids was used. The basis of the method is that the instrument includes an oscillating sample cell; the sample causes a change in the frequency of oscillation corresponding to the density of the sample. The instrument (Paar DMA46 density meter) is calibrated at the test temperature by means of two materials of known density (water and air).

This method is applicable for measuring the density of liquids over a temperature range of 15°C to 38°C and vapour pressures up to 1 MPa. The instrument was first calibrated using the following procedure:

1. The temperature of the sample cell was set. The sample cell was filled with distilled water and allowed to equilibrate for 5 minutes. The instrument output, $T_{(W)}$ was obtained.
2. The cell was cleaned and dried and allowed to equilibrate for 5 minutes and then the meter was read . The instrument output for air, $T_{(A)}$ was obtained.
3. The atmospheric pressure was measured; the density of air, $\rho(A)$, at that pressure and the test temperature and the density of water, $\rho(W)$, at the required temperature were obtained from reference tables.
4. The apparatus constant A was calculated from:

$$A = \frac{T^2_{(W)} - T^2_{(A)}}{\rho(W) - \rho(A)}$$

5. The apparatus constant B was calculated from

$$B = T^2_{(A)} - A \times \rho(A)$$

6. The values of A and B were entered into the instrument, and then the density of doubly distilled water at the test temperature was measured; it should be within ± 0.0001 g/ml of literature values for the density of water at the test temperature.

The density of 2,4-TDI was then determined using the following procedure:

1. The temperature of the sample cell was adjusted to the required value. This was 25°C, being the lowest temperature at which the test substance remained reliable and completely as a liquid. Atmospheric pressure was measured, and the density of air was read from the meter. The difference between the density of air indicated at the meter and the literature value should not be greater than 0.0001 g/ml.
2. The sample cell was filled with 2,4-TDI.
3. The density of the sample was read from the meter.
4. The cell was cleaned, such that the meter showed a value below 0.0012 g/ml for air.

The experiment was performed in triplicate. After determination of the real density, the relative density was also calculated.

2.5 Determination of the vapour pressure of 2,4-TDI (A4)

2.5.1 Estimation of vapour pressure from boiling point

Estimation of the vapour pressure was useful in order to aid choice of the method of measurement. It can also be useful as a means of providing a result when it is considered not necessary to perform a measurement. Estimation by the modified Watson method is described in the description of the A4 test method in the Official Journal.

The modified Watson method[2] to calculate vapour pressure requires knowledge of the boiling point of the test substance, by fitting the following partly empirical equation, valid down to 10^{-5} Pa:

$$\ln P \simeq \frac{\Delta H_b}{\Delta Z_b R T_b} \left[1 - \frac{(3-2T')^m}{T'} - 2m\,(3-2T')^{m-1} \ln T' \right]$$

where
- P = vapour pressure (atmospheres)
- ΔH_b = latent heat of vaporisation (kcal mol^{-1})
- ΔZ_b = a constant (0.97)
- R = the gas constant
- T_b = boiling point (K)
- T' = T/T_b where T is the desired temperature
- m = a constant obtained from the table below
- $\Delta H_b/T_b$ = K_F (8.75 + R ln T_b) where K = 1.01 usually

Choice of m

Physical state	T'	m
Liquid	all	0.19
Solid	>0.6	0.36
Solid	0.6-0.5	0.8
Solid	<0.5	1.19

The method was applied via the program CHEMEST[3].

2.5.2 Measurement

For the determination of the vapour pressure of 2,4-TDI, the static method was used, with two procedures. The first procedure was performed exactly in accordance with the EEC guidelines, using mercury as the manometric liquid.

The clean, dry apparatus was assembled without the test substance, and checked for leaks. Approximately 3 ml of the test substance was put into the sample cell, which was then equilibrated at 23°C, then the vacuum pump was turned on for about five minutes. The purpose of this step was to remove any entrained gas, which could have resulted in a falsely high vapour pressure being found. It was important to ensure that the sample, did not solidify at this stage.

The assembly was then placed in a thermostatted water bath, the temperature of which was measured with a thermometer, and the pressure exerted by the substance at temperatures between 50°C and 88°C was measured. The nitrogen pressure necessary to equalise the two arms of the manometer was measured using a Bourdon gauge. The system background pressure, mBar, determined during the leak check, was subtracted from the nitrogen pressure readings. Several stable readings were taken at each temperature. A linear regression analysis was performed of reciprocal temperature (K) [x value] and the log pressure (Pa) [y value]. From the linear relationship found, the estimated vapour pressure at 20°C was calculated.

The second procedure differed from the first in two respects:

1. Extended pumping at 51.5°C and 0.8 mbar for 2.5 hours was used to remove any trace of impurities.

2. Silicone oil was used as the manometric fluid.

2.6 Determination of the explosivity of 2,4-TDI (A14)

The guideline for Test A14 allows for the full explosivity test to be omitted on reasonable grounds of prior information. The approach used was to study the thermal stability of 2,4-TDI using differential scanning calorimetry (DSC), and compare the results with DSC data for a substance (a tolylene diisocyanate mixture) for which explosivity testing has been performed[4].

DSC records the difference in energy inputs into a substance and a reference, as a function of temperature, while the substance and the reference are subjected to the same controlled temperature programme. This energy is the energy necessary to establish zero temperature difference between the substance and the reference. Processes such as melting, boiling or decomposition may be studied using DSC. Thermogravimetric analysis (TGA) is a complementary technique: the weight of a sample is recorded whilst it is subjected to a controlled heating programme. The weight changes are of use in their own right and can aid interpretation of DSC data.

Equipment (all from Perkin-Elmer).

DSC7 Differential scanning calorimeter.
TGA7 Thermogravimetric analyser.

TAC 7/7 and TAC 7/DX Instrument controllers.
Model 7700 computer with graphics plotter.
Crimper press with a supply of sample pans and lids.

The balance component of the TGA was used to accurately weigh DSC and TGA pans and samples to 0.001 mg.

For DSC and TGA: pans with lids that have a pinhole to allow controlled loss of vapour were used. These are necessary for information regarding boiling.

Methods

Sample preparation

The balance facility of the TGA was used to weigh the sample. Initially an empty pan and lid were placed in the balance and the balance was zeroed. The test substance was added to the pan and a lid was crimped into place. The sample was weighed: 0.5 mg to 3.4 mg of sample was used in either DSC or TGA tests. If the sample was intended for DSC analysis then this weight was noted separately and entered at the system prompt when in the DSC mode.

In TGA mode, the sample pan was placed on the hang-down of the TGA furnace. In DSC mode the sample pan was placed in the left hand well of the DSC furnace and an empty pan, with lid, was placed in the right hand well. The well lids were positioned in the same orientation and the furnace was closed.

Operation, controls and programme

The heaters in each furnace were remotely controlled by a multi-tasking computer. This facility allowed the simultaneous operation of TGA (Task 1) and DSC (Task 2) programmes and the manipulation of stored data (Task 3).

A heating programme was entered into the computer for task 1 and task 2, comprising initial and final temperatures, and the rate of temperature increase. The system was started, and data was obtained on the weight and temperature of each sample. This information was displayed graphically in real-time. At the end of a run the computer calculated changes in mass, enthalpy and temperature, and a print out of these was obtained via a graphics plotter.

Conditions used

Initial temperature:	24°C
Final temperature:	600°C
Heating rate:	20°C/min

3. RESULTS

3.1 Freezing point of 2,4-TDI

Two runs were performed as described in Section 2.2. The results obtained are given in Table 1. Both runs gave a freezing point of 21.0°C, and were acceptable sharp freezing points as defined in Section 2.2.

It was concluded that the freezing point of 2,4-TDI is 21.0°C.

3.2 Boiling point of 2,4-TDI

The Siwoloboff method described in Section 2.3 was used. Two tests using fresh samples of 2,4-TDI were performed. The results obtained were:

	Test 1	Test 2
Start of boiling	254°C	254°C
Re-entry into capillary	252°C	253°C
Atmospheric pressure	1011 hPa	1011 hPa

It was noted that the test substance discoloured slightly above 235°C.

Hence the boiling range of 2,4-TDI is 252°C to 254°C at 1011 hPa. This result is backed up by the estimate of boiling point from DSC, which was 249°C.

3.3 Density of 2,4-TDI

The density meter method described in Section 2.4 was used. The calibration procedure for air and water was satisfactory. Three readings for the density of 2,4-TDI were obtained from the calibrated instrument. These were 1.2141, 1.2140 and 1.2141 g cm^{-3}, at 25°C. The mean of these data is 1.2141 g cm^{-3} (1214 kg m^{-3}), and the relative density compared to the density of water at 4°C (0.99997 g cm^{-3}) is 1.214 (to four significant figures).

3.4 Vapour pressure of 2,4-TDI

3.4.1 Estimation

The method described in Section 2.5.1 was used to estimate the vapour pressure of 2,4-TDI from its boiling point. The result was 1.5 Pa at 20°C.

3.4.2 Measurement

The results obtained by the methods described in Section 2.5.2 are given in Table 2, and are shown in Figure 1. The data are described by the Clausius - Clapeyron equation:

$$\log_{10} VP = B - (A/T)$$

where

VP is vapour pressure (Pa)
T is temperature (K)
B, A are constants

The calculation of B and A by linear regression allow extrapolation to obtain the vapour pressure at 20°C. The results for the two tests were:

	First test	Second test
B	8.91	10.75
A	1965	3056
VP at 20°C (Pa)	158	2.1

These show a large difference due to the effect of extending pumping of the sample. The results from the first test give a value for the product as a whole, whereas those from the second test indicate the vapour pressure of the major component. It is not known why the period of pumping needed to be longer than is usually necessary. The final result is in agreement with prior data[5] (obtained by the gas saturation method, which would not be sensitive to impurities) and with the estimated value, and is therefore preferred.

3.5 Explosivity of 2,4-TDI

The method described in Section 2.6 was followed. The DSC and TGA data for 2,4-TDI are shown in Figure 2 and 3 respectively. They show that, apart from the boiling process, no significant thermal events occurred. For the two DSC runs, the onset temperature for boiling were 248°C and 249°C. TGA showed the onset of the boiling at 189°C and 230°C, with 87% and 71% mass loss, each respectively.

The composition of 2,4-TDI is very similar to that of 80:20 TDI, for which a full A14 explosivity test has been carried out[4]; 80:20 TDI is not explosive, and shows similar DSC/TGA response to that of 2,4-TDI. Therefore, it is reasonable to conclude that 2,4-TDI is not explosive in the sense of the test method A14.

4. DISCUSSION AND CONCLUSIONS

Physicochemical properties of tolylene-2,4-diisocyanate mixture (2,4-TDI) have been determined in accordance with the test methods described in the Official Journal of the EEC(1). The results obtained were as follows:

Freezing point:	(A1)	21°C
Boiling point:	(A2)	252 to 254°C at 1011 hPa
Relative density at 25°C:	(A3)	$D_4^{25} = 1.214$
Vapour pressure (calculated)	(A4)	1.5 Pa at 20°C
(measured)		2.1 Pa at 20°C
Explosivity:	(A14)	Not explosive

The test references are given in parentheses.

The results are consistent with the prior data available for this substance.

REFERENCES:

1. Official Journal of the European Communities, L383A, Volume 35, 29th December 1992.

2. Lyman, W.J., W.F. Reehl, D.H. Rosenblatt, 'Handbook of Chemical Property Estimation Methods', McGraw-Hill. 1982.

3. CHEMEST, Technical Database Services, New York.

4. D.A. Howes, '80:20 TDI, explosive properties', Huntingdon Research Centre, SLL294/942279, within Fisk, P.R., Langner, E.J., 'Tolylene 2,4-/2,6-diisocyanate mixture (80:20-TDI): determination of physicochemical properties', Group External Report, SBER.94.006.

5. Frensdorff, H.K., Adams, R.K., J. Chem. Eng. Data, 20, 13-15 (1975).

Table 1 - Freezing point of 2,4-TDI: run 1

Time (min)	Temperatures (°C)	
	Substance	Bath
0.0	30.0	14
0.5	29.5	14
1.0	29.0	14
1.5	28.5	14
2.0	28.5	14
2.5	28.0	14
3.0	27.5	14.5
3.5	27.5	14.5
4.0	27.0	14.5
4.5	26.0	15
5.0	25.5	15
5.5	25.5	15
6.0	25.0	15
6.5	24.5	15
7.0	24.5	15
7.5	24.5	15
8.0	24.0	15
8.5	24.0	15
9.0	23.5	14.5
9.5	23.5	14.5
10.0	23.5	14.5
10.5	23.0	15
11.0	23.0	15
11.5	23.0	15
12.0	22.5	15
12.5	22.5	15
13.0	22.5	15
13.5	22.5	15
14.0	22.0	15
14.5	22.0	15
15.0	22.0	15
15.5	21.5	15
16.0	21.5	15
16.5	21.5	15
17.0	21.0	15
17.5	21.0	15
18.0	21.0	15
18.5	21.0	15
19.0	21.0	15

Table 1 continued: Run 2.

Time (min)	Temperatures		Time (min)	Temperatures	
	Substance	Bath		Substance	Bath
0.0	20.0	13	16.0	22.0	14.5
0.5	27.5	13	16.5	21.5	14.5
1.0	27.5	13	17.0	21.5	15.0
1.5	27.0	13	17.5	21.5	15.0
2.0	26.5	13	18.0	21.0	15.0
2.5	26.5	13.5	18.5	21.0	15.0
3.0	26.5	13.5	19.0	21.0	15.0
3.5	26.0	13.5	19.5	21.0	15.0
4.0	26.0	13.5	20.0	21.0	15.0
4.5	26.0	14.0			
5.0	25.5	14.0			
5.5	25.5	14.0			
6.0	25.0	14.0			
6.5	25.0	14.0			
7.0	25.0	14.0			
7.5	24.5	14.0			
8.0	24.5	14.5			
8.5	24.5	14.5			
9.0	24.0	14.5			
9.5	24.0	14.5			
10.0	24.0	14.5			
10.5	23.5	14.5			
11.0	23.5	14.5			
11.5	23.5	14.5			
12.0	23.0	14.5			
12.5	23.0	14.5			
13.0	23.0	14.5			
13.5	22.5	14.5			
14.0	22.5	14.5			
14.5	22.5	14.5			
15.0	22.0	14.5			
15.5	22.0	14.5			

Table 2 - Vapour pressure of 2,4-TDI

Test 1: standard conditions		Test 2: extended pumping	
Temperature(°C)	Pressure (mbar)	Temperature(°C)	Pressure (mbar)
50.0	7.5	51.5	0.98
50.5	7.5	55.0	1.18
57.5	10.0	55.0	1.05
58.0	10.0	62.0	1.25
63.0	12.5	70.5	1.40
70.0	15.0	74.0	1.63
76.0	20.0	78.0	1.98
83.0	25.0	81.0	2.07
88.0	30.0	86.0	2.66

In both tests the background pressure was 0.8 mbar.

Each pressure value in the table represents the mean of three readings.

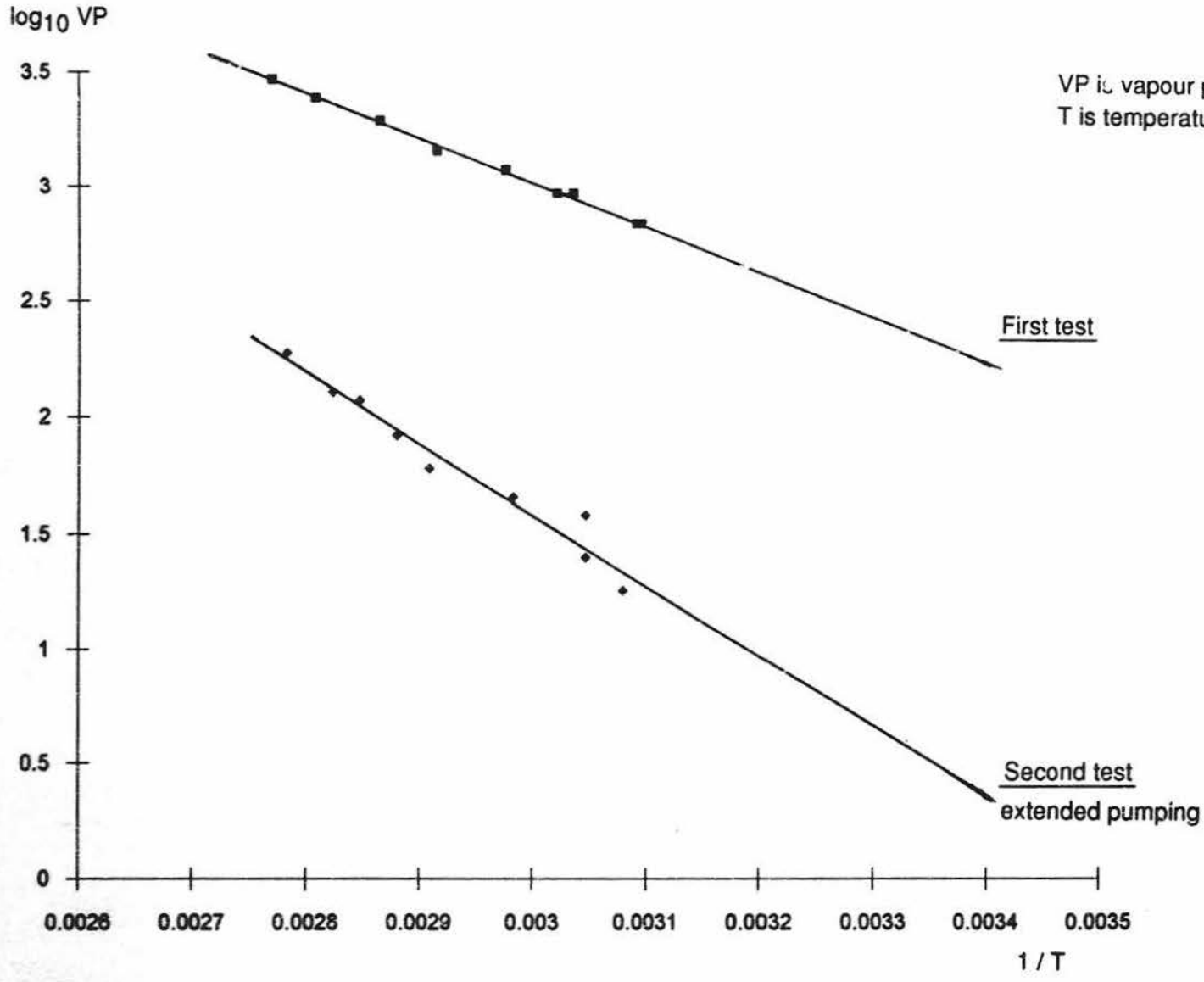
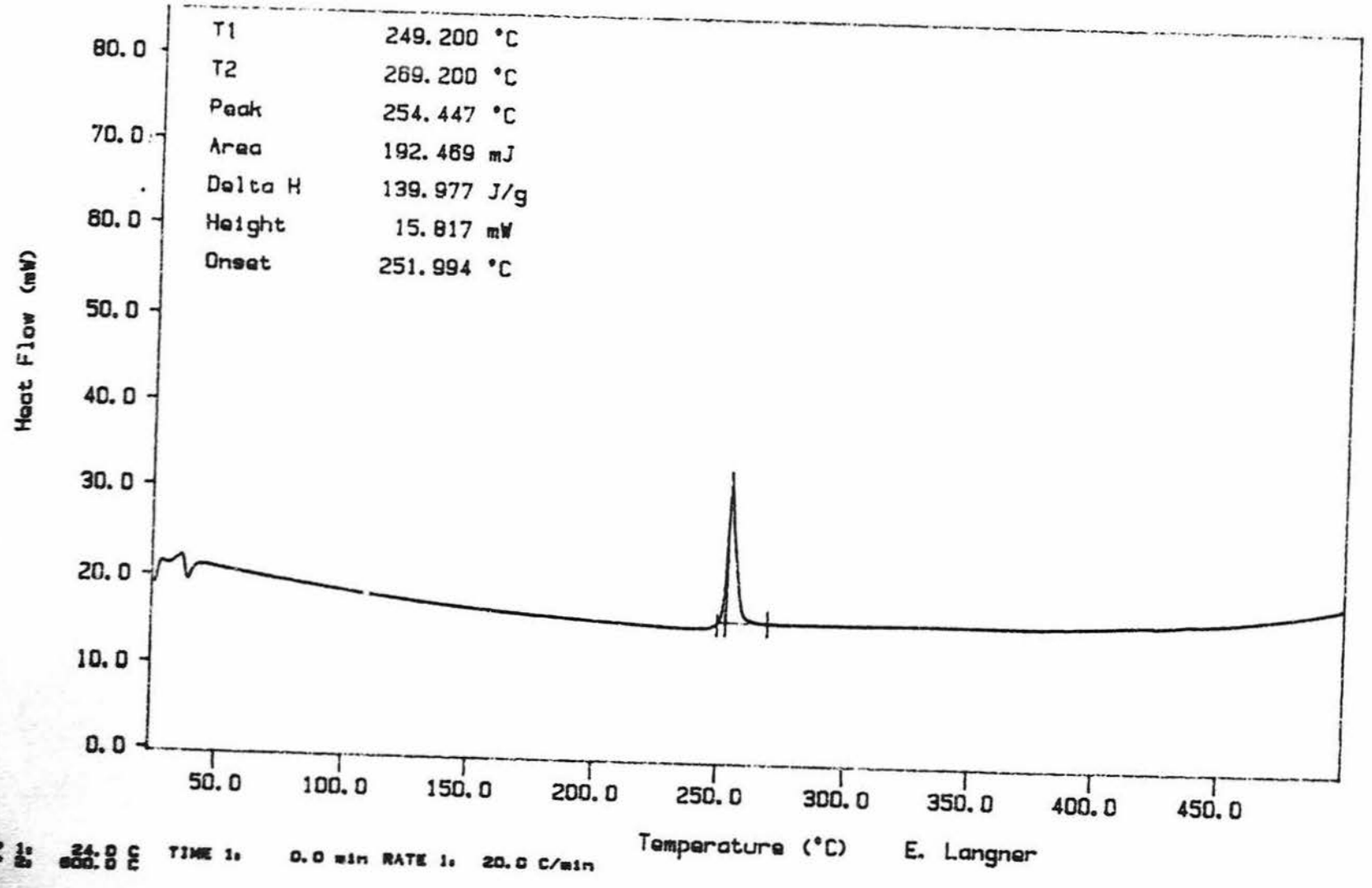


Figure 1 - Vapour pressure of 2,4-TDI

DSC Data File: 0154
Sample Weight: 1.375 mg
Wed Mar 02 13:53:13 1994
st94/015 6205 2/3/94 file=0154

PERKIN-ELMER
7 Series Thermal Analysis System



TEMP 1: 24.0 C TIME 1: 0.0 min RATE 1: 20.0 C/min
TEMP 2: 600.0 C

Figure 2 - DSC of 2,4-TDI

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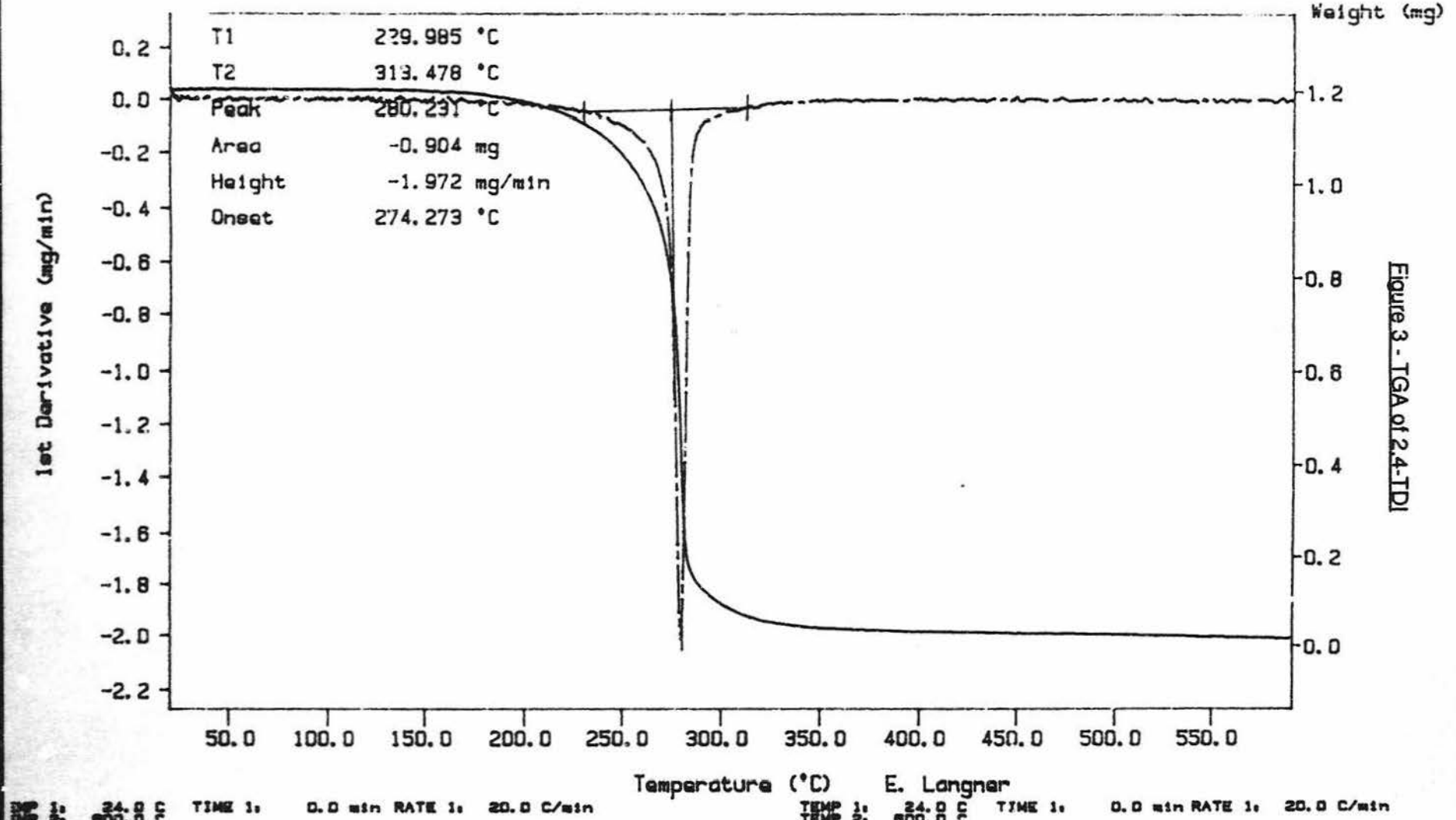
GA 1st Derivative: 0153
ample Weight: 1.279 mg
ed Mar 02 13:51:46 1994
st94/015 6205 2/3/94 file=0153

PERKIN-ELMER
7 Series Thermal Analysis System

TGA File Name: 0153
Sample Weight: 1.279 mg
Wed Mar 02 13:51:46 1994
st94/015 6205 2/3/94 file=0153



TEMP 1: 24.0 C TIME 1: 0.0 min RATE 1: 20.0 C/min
TEMP 2: 600.0 C

TEMP 1: 24.0 C TIME 1: 0.0 min RATE 1: 20.0 C/min
TEMP 2: 600.0 C

Figure 3 - TGA of 2,4-TDI

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APPENDIX A

Study Protocol

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MASTER PROTOCOL

TITLE: Determination of the physicochemical properties of a series of isocyanates

PURPOSE AND SCIENTIFIC OBJECTIVE: To provide values of physicochemical properties for regulatory purposes.

STUDY DIRECTOR: P.R. Fisk

STUDY DESIGN: The master protocol for the study lists the complete range of tests that will be needed within the study. Protocol supplements will list the test substance details and the specific tests necessary for that substance.

TEST SUBSTANCES: The test substances will be obtained from the International Isocyanates Institute, *via* the SRC Compound Control Unit.

REFERENCE SUBSTANCES: Any reference substances necessary will be obtained from reliable sources, *via* the SRC Compound Control Unit.

DATA:
Data will be generated and stored in compliance with GLP.

QUALITY ASSURANCE:
The study will be audited by the SRC Quality Assurance Unit.

REPORTING: The results will be presented as an External Report, one report for each substance.

SAFETY: Normal safety procedures will be observed. A copy of the test substance safety data sheet will be kept in the study file in the laboratory.

ACCEPTED
STUDY DIRECTOR P. R. Fisk DATE 2/2/94

APPROVED FOR
SHELL
RESEARCH LIMITED C. L. Dubin DATE 3/2/94

IF DRAFT PROTOCOL, DATE COMMENTS REQUIRED BY _____

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MASTER PROTOCOL

PROTOCOL SUPPLEMENT REQUIREMENTS:

A protocol supplement will be issued for each study. The following information will be included:

- study number
- title of study
- proposed start and report dates
- details of the test substance
- the tests required, selected from the list in the MASTER protocol

TESTS REQUIRED AND METHODS:

The list below gives the SRC Standard Operating Procedures that will be used in the study. Further information on how each one will be applied in the study are given below.

SOP no.	Title	EEC test no.
401	Melting point	A1
431	Freezing point	
404	Boiling point	A2
420	Density	A3
403	Vapour pressure (gas saturation)	A4
428	Vapour pressure (static method)	
402	Differential thermal analysis	(A14)
436	Differential scanning calorimetry	
430	Flash point	A9
519	Autoflammability of liquids	A15
610	Autoflammability of solids	A16
441	Estimation of properties by calculation	

Estimation of physicochemical properties by calculation

For certain regulatory purposes it is permissible to present physicochemical properties as estimated results. This approach will be used in the study. In all cases estimated values will be validated by comparison with measurements on relevant analogues, either from within the study or from published literature.

Thermal stability testing

The performance of differential scanning calorimetry (DSC) as the first test on any of the test substances is an essential step in the study. The DSC experiment provides information regarding melting, boiling and thermal stability. Thermogravimetric analysis will be performed also, in order to gain information about any mass losses occurring during heating. Together, the tests are referred to as thermal analysis. The potential explosivity properties of the substances will be considered from these tests. For at least one test substance, a full explosivity test will be performed according to EEC Test A14. This will be done at Huntingdon Research Centre, and reported as an appendix in the appropriate SRC report.

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Melting point and freezing point

For solids, melting point/range will be studied using the capillary method backed up by the DTA work.. For liquids, freezing point is appropriate. The tests will comply with the EEC guidelines.

Boiling point

The Siwolobov method will be used. The tests will comply with the EEC guidelines.

Density

Automated methods will be used, for both liquids and solids. The tests will comply with the EEC guidelines.

Vapour pressure

Initial investigations of all the test substances for which measurement is required will be made using the static method. If the vapour pressure is below the usable range of that technique, the gas saturation method will be used if possible. The gas saturation technique is not suitable for complex mixtures; if the pressure is low and the substance is a mixture then alternative techniques will be used *via* a contract study reported as an appendix in the appropriate report. The tests will comply with the EEC guidelines.

Flash point

This test is only appropriate to liquids or low melting point solids. For solids, they will be introduced to the apparatus as melts, or weighed solid particles will be dropped in, provided the melting range is below the usable range of the apparatus. The tests will comply with the EEC guidelines.

Autoflammability

Tests A15 or A16 will be used for liquids and solids respectively. For low melting solids which are not autoflammable as solids, the test substance will be used as a melt provided it can be handled satisfactorily. The tests will comply with the EEC guidelines.

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MASTER PROTOCOL: AMENDMENT NUMBER 1

TITLE: Determination of the physicochemical properties of a series of isocyanates

MODIFICATIONS AND JUSTIFICATION

Tests of thermal stability will be performed according to SOP436, 'Differential scanning calorimetry and thermogravimetric analysis'. Two runs on each substance requiring testing will be performed, unless the results indicate that further testing is needed.

This clarification is needed because SOP402 (differential thermal analysis) is mentioned in the protocol but will not be used, and because SOP436 has been extended to include thermogravimetric analysis.

ACCEPTED

STUDY DIRECTOR P R. Fisk DATE 21/2/94

APPROVED FOR SHELL RESEARCH LIMITED C. L. Dubre DATE 21/2/94

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PROTOCOL SUPPLEMENT

(to be read in conjunction with MASTER PROTOCOL entitled 'Determination of the physicochemical properties of a series of isocyanates')

Project Letters - Experiment Number

P P D 6 2 0 5

TITLE: Tolylene-2,4-diisocyanate (2,4-TDI): determination of physicochemical properties

STUDY DIRECTOR: P.R. Fisk 2588

TEST SUBSTANCE:

Name	Tolylene-2,4-diisocyanate
Source	Rhone-Poulenc, France
Purity/composition	Supplied as the commercial product SCURANATE T100, batch 93 363 0501 (purity 99.9
Expiry date for use	10th August 1994
SRC Code	ST94/015

TESTS REQUIRED:

Test	Comment
Freezing point	
Boiling point	
Density	
Vapour pressure	Measured
Thermal analysis	

START DATE: February 17th 1994. **PROPOSED REPORT DATE:** July 1994

ACCEPTED
STUDY DIRECTOR PRFish **DATE** 16/2/94

APPROVED FOR SHELL RESEARCH LIMITED CR Dubre **DATE** 16/2/94

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AUDITED BY [signature] **ON** 16-2-94 **AUDIT REPORT NO.:** /

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APPENDIX B

Description of the test substance

The test substance was provided from Rhone-Poulenc as the commercial product SCURANATE T100, via the Test Substance Unit, with the following description and data:

Name:	Tolylene-2,4-diisocyanate
CAS No.:	584-84-9
Purity/composition:	99.9% TDI (99.4% 2,4-TDI, 0.6% 2,6-TDI)
Batch Number:	933630501
Date of manufacture:	29-12-93
Colour (Hazen):	10
Acidity (expressed):	1mg HCl/kg
Hydrolysable chlorine:	1 mg/kg
Total chlorine:	1 mg/kg
Dimer:	< 200 mg/kg
SRC Code:	ST94/015
Expiry date:	13th March 1996

The following relevant typical physical and chemical data were also provided with the sample by the supplier:

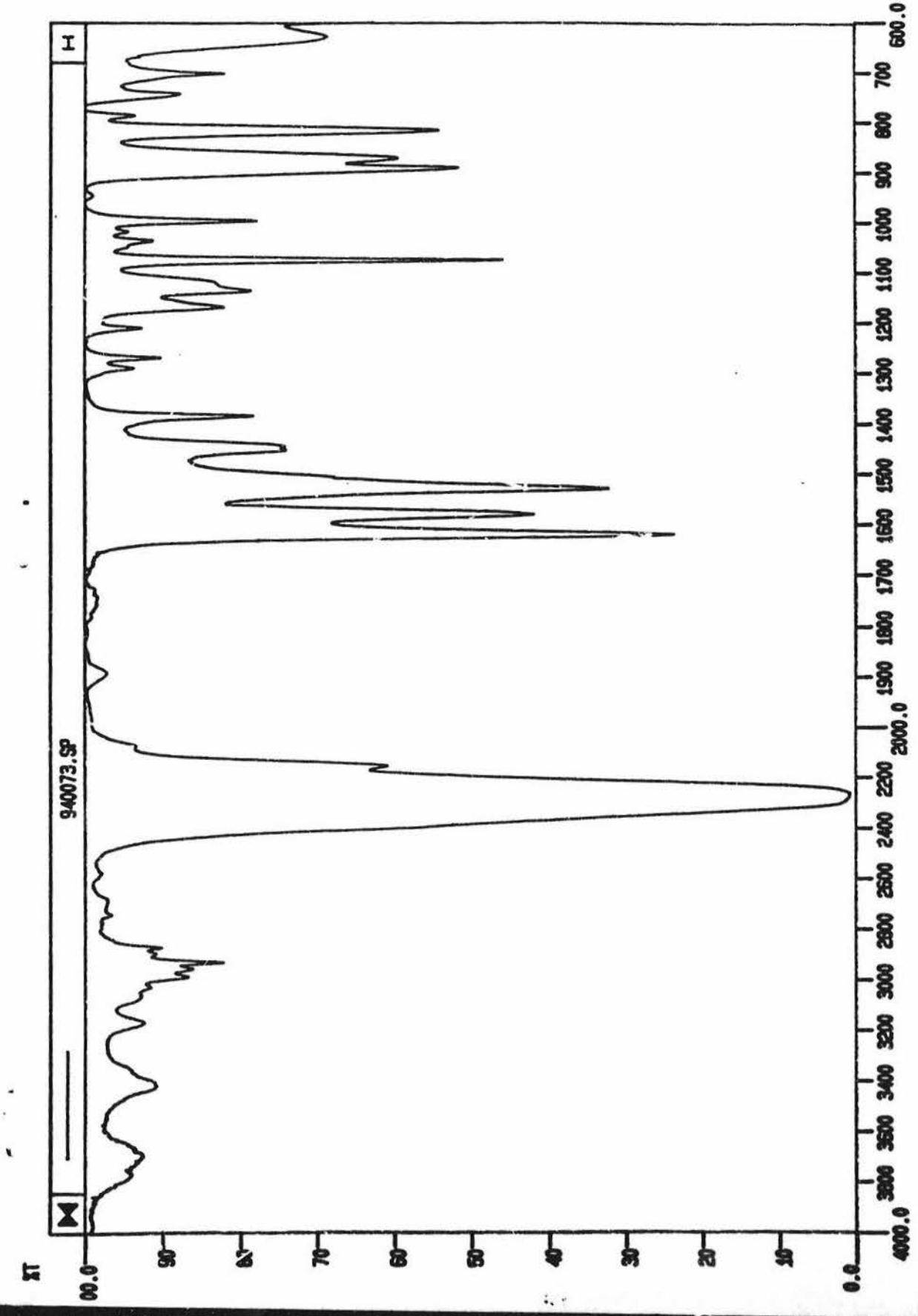
Density:	1.22 g/cm^3
Boiling point:	250°C at 1013 hPa
Vapour pressure at 25°C:	0.033 hPa
Kinematic viscosity at 25°C:	3 mPa s
Crystallization point:	21.5 - 22°C:
Vapour density (air = 1):	6

No claim of GLP compliance is made in respect of the above property data, provided by the supplier of the test substance.

Characterisation

Characterisation tests were performed by the TSU. Measurements of its IR spectrum were made on 11 February 1994 (Figure B.1) and on 13 March 1995. The spectra were found to be identical. Therefore the stability of the substance during the study was confirmed.

Figure B.1: IR spectrum of 2,4-TDI



FURTHER DETAILS FOR DATA BASE ENTRY

INDEX TERMS: 10. Chemicals
16. Research and Development

KEYWORDS: Freezing, boiling, density, vapour pressure, explosivity, isocyan[illegible]

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Tolylene-2,4-diisocyanate (2,4-TDI): **Determination of physicochemical properties**

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